Highly Crystalline Mesoporous Titania Films from Self-Assembled Nanocrystalline Building Blocks for Photovoltaic Applications

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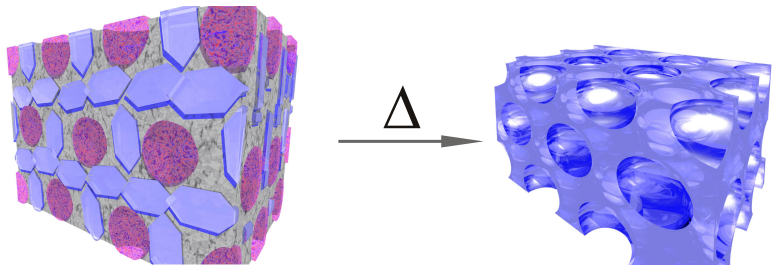
Nanostructured films of TiO_2 have enormous potential for applications in photovoltaics and energy storage. However, reaching this potential requires films that simultaneously feature both large and easily accessible surface area and highly crystalline pore walls. Crystalline titania layers are most commonly assembled from crystalline particles by sintering, but this approach is limited concerning the possibility to tune the structure and porosity. Templated sol-gel processes are used to overcome these shortcomings, but the crystallinity of the resulting TiO_2 frameworks is usually only moderate.

Recently, we developed a new preparation strategy combining the advantages of both techniques by fusing pre-formed titania nanocrystals with surfactant-templated sol-gel titania, which acts as a structure-directing matrix and as a chemical glue.[1] This technique can be described as a "brick and mortar" approach, in which the “mortar” acts as a reactive precursor for the further growth of the crystalline phase seeded by the nanocrystalline “bricks” (Scheme 1). This synergy leads to a lowered temperature needed for crystallization and to the preservation of the mesoporous structure. Different nanoparticle precursors emerging from non-aqueous sol-gel processes were studied for this approach. Specifically, microwave assisted nanocrystal synthesis was successfully employed to simplify and shorten the synthesis process. The thin films were characterized using *in-situ* 2D-GISAXS, WAXS and TEM measurements to monitor and visualize the seeding effect, crystal growth and mesostructure development during the calcination.



Scheme 1. Scheme of formation of crystalline mesoporous titania films (right side) via the “brick and mortar” approach. The nanocrystalline titania “bricks” (light blue, left side) are dispersed in amorphous titania “mortar” (grey), which is periodically self-assembled around the micelles of the polymer template (magenta).

Coatings with a broad variety of periodic mesostructures and pore sizes that are tunable by varying the fraction of the “bricks”, and thicknesses ranging from few nanometers to several micrometers are accessible using the same organic surfactant template (Figure 1).

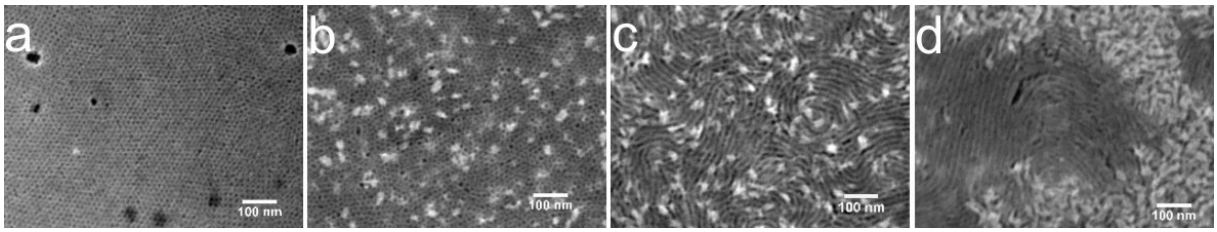


Figure 1. a) SEM micrograph of a calcined film made from a coating solution consisting of 0 % TiO_2 particles and 100 % Ti sol-gel precursor, b) 10 % particles and 90 % sol-gel, c) 30 % particles and d) 50 % particles.

These mesostructured and crystalline films are employed as active layers in dye-sensitized solar cells, and the beneficial combination of crystallinity and porosity enables the preparation of mesostructured and crystalline films which exhibit a conversion efficiency of 6.0 % at only 2.7 µm thickness. This is impressively high for such thin films in combination with a non-volatile electrolyte and an organic dye, showing the advantage of nanostructured electrodes for electron and electrolyte diffusion, and makes them promising candidates for photoanodes in dye-sensitized solar cells (Figure 2).

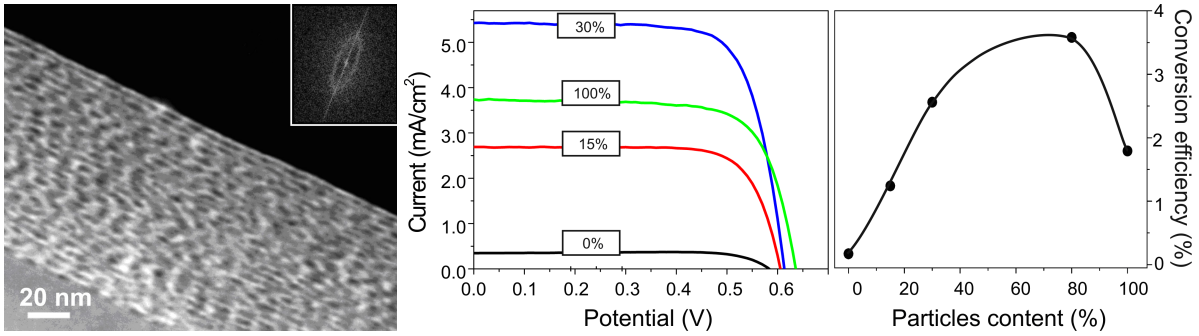


Figure 2. Left: Cross-sectional STEM-HAADF image of a film made from 50 % nanoparticles and Fourier transform of the picture revealing the periodic pore structure (inset). Middle: Photocurrent-voltage curve of "brick and mortar" titania layers with varying nanoparticle content. Right: Dependence of conversion efficiency of DSC devices on the nanoparticle content of the "brick and mortar" titania layers (Layer thickness 1.0 µm, D205 sensitizer and Z646 non-volatile electrolyte).

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(1) Johann M. Szeifert, Dina Fattakhova-Rohlfing, Dimitra Georgiadou, Vit Kalousek, Jiri Rathouský, Daibin Kuang, Sophie Wenger, Shaik M. Zakeeruddin, Michael Grätzel and Thomas Bein, *Chem. Mater*. **2009**, *21* (7), 1260–1265.